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INTERCONNECTION AND ENCAPSULATION OF INTEGRATED CIRCUITS BY ANODIC BONDING

Quarterly Progress Report No. 2

Period Covered 1 October - 31 December 1966

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINSTRATION

Contract No. NAS 12-142

NASA
ELECTRONIC RESEARCH CENTER
575 Technology Square
Cambridge, Massachusetts 02139

Attn: CQ/Qualifications and Standards Laboratory

P.R. MALLORY & CO., INC.
Laboratory for Physical Science
Northwest Industrial Park
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I. INTRODUCTION.

Work during the first quarter had established that silicon diodes metallized by aluminum according to Fig. 1 could not be hermetically encapsulated by means of our proprietary technique because the various metal and oxide steps could not be filled in with available glasses at temperatures below the silicon-aluminum eutectic. Accordingly, during a part of the first quarter, we commenced work on a high temperature metallization with the following requirements.

a. Metal can be brought into good ohmic contact with silicon.
b. At the bonding temperature the metal must not react with silicon in such a way as to damage the electrical properties of the junctions.
c. Metal must adhere to silicon dioxide.
d. Metal must have acceptable sheet resistance
e. Metal must be suitable for photolithographic processing.
f. Metal can bond to glass.

It was considered that a sandwich structure would be required in order to satisfy all of the above requirements, and as a first try we worked on a molybdenum-chromium composite which was expected to meet all requirements except d. Procedures for the sequential deposition of the metals by sputtering were worked out and a start was made at pattern delineation by photolithographic techniques.

During the second quarter further work on high temperature metallization was done. During the fourth month of the contract the molybdenum-chromium metallization was found to be unsatisfactory after bonding at high temperatures. Hence, experiments on a molybdenum-aluminum sandwich were started.

During the fifth month the effect of bonding on the molybdenum-aluminum metallization was investigated in some detail. In particular it was found that the metallization tended to damage the electrical properties of the diodes and that further damage resulted from bonding. Furthermore, bonding appeared to increase the sheet resistance of the films by large amounts.

During the sixth month the reasons for several of these difficulties were diagnosed, and steps were taken to correct them. The effect on the electrical characteristics of bonding metallized diodes to non-metallized glass was determined. Problems in etching the molybdenum-aluminum sandwich were traced to the molybdenum having been sputtered in an argon atmosphere of insufficient purity.

This report summarizes two months' work carried out by 1 1/4 professionals over a three month period.

II. MOLYBDENUM-CHROMIUM METALLIZATION.

When we commenced work on high temperature metallization, it was apparent that with available glasses an encapsulation temperature in excess of 600°C would be required. The plan was to utilize ultimately a three layer structure with the following properties. A first layer to contact the silicon without deterioration of electrical properties; a second layer, probably a noble metal, to give the structure a low sheet resistance; and a third layer which bonds to glass. For the first layer we picked molybdenum which according to the phase diagrams should not interact with silicon below 1400°C. For the third layer we considered chromium which had previously been bonded to several glasses in the temperature range 350-500°C.

As a temporary measure, it was decided to first investigate the molybdenum-chromium system. Sequential metallization and pattern delineation were carried out according to the procedures described in the first Quarterly Report. Test vehicles were silicon diodes of the geometry shown in Fig. 1. The diodes used in these early trials had poor electrical characteristics so that electrical effects of metallization and bonding were not evaluated.

The metallized diodes were bonded to #7740 and also to #7070 glass. The bond between either glass and the chromium lines was considered to be poor, bonding failure apparently being due to excessive oxidation of the chromium above 500°C. Experimentation with different bonding temperature cycles did not lead to any substantial improvements in bondability. Furthermore, it was difficult to make electrical contact to the chromium-molybdenum lines subsequent to bonding. In view of the above difficulties, it was decided to stop work on the chromium-molybdenum system in favor of an aluminum-molybdenum system which is discussed in the following sections. The latter system was selected for the following reasons.

1. With molybdenum acting as a barrier between the silicon and the aluminum the system should be suitable for work above the silicon aluminum eutectic of 574°C, the upper limit being the meling point of aluminum (660°C).

2. Aluminum was known to bond to glasses at high temperatures.

3. For equal film thickness, the sheet resistance of the molybdenum-aluminum system is of course much lower than that of the molybdenum-chromium system.

4. The etching should not present any problems.

III. THE MOLYBDENUM-ALUMINUM SYSTEM, DEPOSITION AND ETCHING.

The molybdenum-aluminum metallization is deposited in the following manner. The sputtering system is pumped down to less than 5×10^{-6} torr and argon is admitted to a pressure of about $1-2 \times 10^{-4}$ torr. Molybdenum is presputtered on a shield for 30 minutes and then sputtered onto the substrate for 15 minutes to produce a shiny film of a thickness of about 1000 - 1500 Å. Without breaking the vacuum aluminum is then presputtered for an hour and sputtered onto the substrate for 30 minutes. The aluminum film has a considerably rougher texture than the molybdenum film; its thickness is about 4500 Å. During both depositions the substrate is at a temperature of approximately 200°C because of radiation heating from the targets. The resistivities of the two films are of the order of 30 μ ohm cm for the molybdenum and 3-6 μ ohm cm for the aluminum. It is evident, therefore, that almost all the current is conducted in the aluminum film.

Patterns are etched into the molybdenum-aluminum films by photolithographic techniques. The aluminum is etched in a solution containing one part of 50% NaOH and two parts alcohol. The molybdenum etch contains one part HNO_3, one part H_2SO_4 and three parts water. The molybdenum etch attacks the aluminum only slowly so that the latter acts in effect as a mask.

Usually the etching proceeds in a straight forward fashion. However, during the last weeks of the sixth contract month the molybdenum etched in some cases far slower than usual and in other cases did not etch at all.

After some experimentation it was discovered that this was due to the fact that the molybdenum had been sputtered in the presence of an air leak in the argon line. It was also observed that even without a leak the molybdenum etched faster if the sputtering was done in a system that was protected by a liquid nitrogen trap. It is of interest that the lack of etchability was not simply an oxidation effect as demonstrated by the following series of experiments, all performed at the time the air leak was present in the sputtering system.

1. When the molybdenum and aluminum were sequentially deposited on pyrex, the former etched at the normal rate.

2. When only molybdenum was sputtered onto silicon, it etched though perhaps somewhat slower than usual.

3. When molybdenum and aluminum were sequentially deposited on silicon, the former etched very slowly or not at all as noted above.

4. When only molybdenum was deposited on silicon, and the wafer was then exposed to the heating cycle characteristic of the aluminum deposition, the molybdenum etched very slowly or not at all.

It would seem therefore that molybdenum, sputtered in a low purity argon atmosphere, reacts with the silicon such as to form a non-etchable species. The reaction depends apparently on temperature and time.

IV. EFFECT OF Mo-Al METALLIZATION ON DIODE CHARACTERISTICS.

Initial work with the Mo-Al metallization was done on diodes whose junction characteristics were so poor that no electrical evaluation could be made. The next time the metallization was tried out on diodes with initial breakdown voltages of about 200 volts. After metallization the breakdown voltages were reduced to the 20-70 volt range. At least some of the deterioration could be accounted for by shorts of the metal pads to the silicon through pin holes in the planar oxide. However, in view of the prevalence of breakdown voltages after metallization of the order of 40 volts there was concern that the planar oxide as grown in our furnaces might not be capable of supporting appreciably higher voltages. In order to check this point metallization patterns were deposited on oxidized silicon slices which had not been further processed. The oxide thickness on these slices was the same as on the above diodes, i.e. 1μ. Dielectric breakdown of the oxide was determined by probe measurements using a curve tracer as the power supply. Results of these measurements are shown in table 1. It will be noticed that in the majority of cases, breakdown occurred above 350V. A breakdown below 100V was found only near the edge of a slice. Therefore, our oxide had in general a dielectric strength in excess of 3×10^6 V/cm which is in agreement with published values.

In view of these results, it was felt that almost all of the deteriorated junction characteristics were due to pin holes in the oxide which had evidently resulted from faulty KPR work.

In order to correct the problem, new photolithographic masks were ordered, and a new batch of diodes was made. Visual observation indicated that these diodes had a far better oxide than the first batch, pinhole density being reduced by several orders of magnitude. The diodes were metallized as previously. Data on reverse characteristics before and after metallization are shown in table 2. They indicate that the Mo-Al metallization does not significantly damage the reverse characteristics of the junctions.

V. EFFECT OF BONDING ON RESISTANCE OF METAL LINES.

Metallized diodes were bonded at 630°C to #7070 glass plates with matching aluminum metallization as per fig. 1. Gold plated kovar was alloyed to the backsides of the diodes and the forward characteristics of the diodes were measured by a four-probe technique. Current-voltage plots representative of the range of results are shown in fig. 2. In general it was deduced that the diodes had series resistances in the range of 10 to 50 ohms. From earlier work it was evident that so high a resistance was unlikely to originate at the silicon-molybdenum interface. Rather it was suspected to arise either in the metal lines themselves or at the interface between the Mo-Al pad on the silicon oxide and the aluminum line on the glass.

In order to further investigate these effects the test vehicle shown in fig. 3 was designed. It consists of an oxidized silicon chip with three sputtered Mo-Al lines A, B and C. Oxide thickness, line thickness and line width all correspond to those we are using on the diodes. To the silicon chip is bonded a glass chip with one aluminum line D such that D overlaps the lines A, B and C. Every effort was made to duplicate the conditions that are found in the encapsulation of the diodes.

Masks for the test vehicle were fabricated and several units assembled. The sheet resistance of the four lines was measured before bonding, after bonding at 550°C and after a second bonding operation at 630°C, the latter being the bonding temperature for the diodes.

The bonded test vehicle was approximated by the equivalent circuit shown in fig. 4. Though this is only a rough approximation for a far more complex situation it serves to show up gross resistance changes during bonding.

The overlap resistances are calculated in the following manner. By applying current at A_1 and A_4 and measuring the voltage between A_2 and B_2 one derives the resistance R_A. Similarly one can determine R_B, R_C, $(R_D)_1$, $(R_D)_2$ and the sum

$(R_D)_0 + (R_D)_3$. In addition one measures the resistance in the following loops:

$$R_A + R_{AD} + (R_D)_1 + R_{BD} + R_B$$

$$R_A + R_{AD} + (R_D)_1 + (R_D)_2 + R_{CD} + R_C$$

$$R_B + R_{BD} + (R_D)_2 + R_{CD} + R_C$$

Thus, one obtains three equations with three unknowns the latter being the overlap resistances R_{AD}, R_{BD} and R_{CD}.

Probably the most significant results derived from these experiments was the observation that after bonding the lines were shorted to the silicon. On the other hand, when glass without metallization was bonded to the metallized silicon chip under similar conditions no shorting was observed. The implication is that the metal line D on the glass shorts to the silicon at the edges of the chip. This occurs because of chipping of the silicon oxide during scribing. In the next section we shall describe efforts to overcome this problem.

Measurements of the resistance (R_A, R_B and R_C) and overlap resistance after bonding at 550°C and after re-bonding at 630°C gave the following range of results.

	550°C	630°C
Line resistance	.090 - .145 $\Omega/\square$	.140 - .250 $\Omega/\square$
Overlap resistance	.075 - .365 $\Omega/\square$	.100 - 1.28 $\Omega/\square$

The line resistance after the 550°C bonding treatment (at which steps were not filled in) was essentially equal to the initial line resistance.

Another result of these experiments was the observation that the resistance of $(R_D)_0 + (R_D)_3$ increased by a large factor during bonding. At least in part this is believed to be due to the alloying of the silicon with the aluminum line at the edges of the chip. However, there was concern that an additional resistance increase might result from the diffusion of aluminum into the glass or from the oxidation of the aluminum under bonding conditions. To check this, metallized glass was placed on a molybdenum sheet and exposed to bonding conditions. As expected, no bond resulted. Data on the line resistance before "bonding" and after "bonding" for various lengths of time are shown in table 3. The table demonstrates that for bonding operations lasting less than 10 minutes, resistance changes of less than 25% are to be expected. Thus, migration of the aluminum into the glass presents apparently only a minor problem and effects due to oxidation are negligible.

In view of the above, the occasionally observed large increases in R_A, R_B and R_C during bonding might be attributed to mechanical damage of the respective lines by the sharp edges of the glass. This is a problem only with the test vehicle of fig. 3 and not with the diodes of fig. 1. Hence, it need not concern us any further.

Further study of earlier reported data regarding the resistors $(R_D)_1$ and $(R_D)_2$ as well as the overlap resistances throw some doubt on their validity. So as to clear up these points a new geometry has been designed which is shown in fig. 5. It will be seen that the new geometry will allow a far more straightforward determination of sheet resistance. Furthermore, the overlap resistances in fig. 5 are in line as in the diode configuration of fig. 1 rather than at right angles as in fig. 3.

As a further check on the above conclusion that oxidation changes the resistance of the aluminum lines by negligible amounts, we attempted to bond the test vehicle of fig. 3 in an argon atmosphere. It was argued that if oxidation were indeed of little importance then the same resistance changes should occur in argon as in air. On the other hand if oxidation had an appreciable effect then the resistance changes should be much smaller in argon than in air. Contrary to expectations we found that satisfactory bonds could not be made in argon and that the lines tended to be damaged during the bonding attempts. Hence, no meaningful resistance measurements could be made on the argon-bonded units. The reason for partial bonding failure was traced to the particular experimental conditions.

VI. BEVELLING OF DICE.

In the previous section it was reported that the aluminum line on the glass tended to contact the silicon at the edges of the dice where the oxide had been chipped by scribing. This, of course, results in shorted junctions. One method by which this difficulty can hopefully be removed is illustrated in fig. 6. Prior to processing, a network of grooves is etched into the silicon. The silicon is then processed in the usual way and finally diced in the centers of the grooves. As a result the chip has the bevelled appearance of the figure. It is hoped that any damage to the oxide will be confined to the bottom of a groove where it cannot be contacted by the aluminum lines on the glass.

In pursuance of this program, work has been done on the photolithographic etching of silicon. It soon was found that KTFR or KMR will not mask sufficiently long to permit removal of a significant amount of silicon (the goal is 5-10 μ) with the usual HNO_3, HF etches. It was therefore decided to use a metal mask in place of the photo resist mask. After some trials, chromium was found to be practically inert to a 10:1 HNO_3, HF etch. The etching of chromium by photolithographic techniques presented some difficulties. In the third contract month we had etched the chromium in concentrated HCl at about $80^{\circ}C$. The etching time, however, is only of the order of seconds and very critical if the integrity of the photoresist is to be preserved. Therefore, we have been experimenting with a milder etch which was obtained from Electronic Films, Inc.

If these trials work out satisfactorily, a new lot of diodes with tapered chips will be made and the configuration of fig. 6 will again be tried out at a later date.

VII. FILL-IN OF STEPS.

A goal of this contract is to produce a hermetic package in which the active silicon region is in contact with glass. As a consequence it is essential for the glass to fill-in the various metal and oxide steps on the surface of a silicon chip.

Using #7070 low alkali glass, the oxide steps fill-in readily at 630°C, as judged by visual observation. By the same criterion the steps formed by metal lines on the glass also fill-in, though less rapidly. The steps due to the metallization on the silicon however do not seem to fill-in completely. Nor could the steps apparently be filled at temperatures as high as 700°C where the aluminum is liquid. On the other hand, metal steps of greater height have been successfully filled in on other semiconductor devices. In view of these apparently contradictory results we have come to question whether visual observation is a valid criterion. It could be that in certain step geometries the bonded glass reflects light in such a way that contrary to fact a step appears not to have bonded.

In order to clear up this point, we are planning to complement the visual observations with hermeticity tests.

VIII. EFFECT OF BONDING ON DIODE CHARACTERISTICS.

In view of the above described shorting of the metal line on the glass to the silicon chip further work on the geometry of fig. 1 has been temporarily halted. Following a suggestion by the contractor, we instead investigated the configuration shown in fig. 7. Here, the metallization on the silicon chip is extended further over the oxide and a non-metallized glass plate is bonded to the structure in such a way that the junctions are covered but a part of the metallization on the silicon oxide is left uncovered. Thus, electrical testing after bonding is feasible.

Bonding was done in room air at a temperature of 630°C for about 3 minutes. For the most successful bonding operation to date, a comparison of the reverse characteristic before bonding, after bonding and after a heat treatment at 630°C for 15 minutes is shown below.

	I/60V na	I/80V na	I/120V na	BV volts
Before bonding	12	15	21	160
After bonding	22	32	100	150
After heat treatment	7	11	40	140

A slight reduction of breakdown voltage, a somewhat lower leakage at low voltage and a somewhat higher leakage at high voltages is generally observed. Similar results were obtained many months ago with non-metallized diodes. In order to investigate whether the change in reverse characteristic was associated with the temperature at which bonding was performed a few diodes were exposed to the equivalent temperature cycle without glass being bonded to them. On the "best" diode the following results were obtained.

	I/20V	I/40V	I/60V	I/80V	I/100V	I/120V
				na		
Initial	9	13	20	40	110	360
First heating cycle	11	19	27	40	56	86
Second heating cycle	8	12	16	22	32	46
Third heating cycle	6	11	20	50	180	500

The first two heating cycles consisted of 5 minutes each at 630^{o}C. During the third cycle the diode was exposed to 630^{o}C for 15 minutes. The above data show that heat treatments by themselves produce substantial changes in the electrical characteristics. However, it is probable that not all the changes during bonding can be accounted for by the heating cycle.

On a few occasions it was observed that bonded diodes with good characteristics became partially shorted when they were heated at 630^{o}C for periods in excess of 15 or 20 minutes. It is suspected that this effect is associated with a reaction of the metallization with the planar SiO_2. Another effect that is not well understood is concerned with relaxation phenomena subsequent to bonding. First measurements after bonding are made as soon as a diode reaches room temperature. At this time the diode is usually leaky and has a low, soft breakdown. The characteristic steadily improves with time and reaches a stable value after about 15 to 20 minutes.

A few diodes were alloyed to gold plated Kovar strips, and their forward characteristics were measured by means of four probes. Results on five diodes are shown below.

I_f in ma #	V_f volts 1-10-5	V_f volts 1-10-1	V_f volts 1-16-A	V_f volts 1-16-B	V_f volts 1-16-C
1	.58	.62	.61	.62	.60
3	.64	.71	.69	.68	.67
10	.72	.85	.85	.79	.83
30	.81	1.04	1.20	1.05	1.16
100	.95	1.46	1.87	1.65	1.90
170	1.08				
R_S (ohms)	1.7	6.3	9.5	8.7	11.2

In the last line of the table estimated series resistances are shown. These data represent a substantial improvement over earlier reported data obtained on the geometry of fig. 1 where series resistances between 10 and 50 Ω were observed. However, even the lowest of the above forward voltage drops is far from satisfactory. Of the total estimated series resistance of 1.7 Ω probably less than .5 Ω represents the resistance of the metallization. The remaining resistance would seem to occur either at the silicon-gold contact, at the molybdenum aluminum contact or at the silicon-molybdenum contact. This matter will be further investigated.

It should be understood that the above results are based on relatively few trials. It is encouraging that bonded diodes with rather good electrical characteristics could be obtained in our first attempts. Obviously, a large amount of work will be required to optimize the bonding procedure with respect to the electrical characteristics.

IX. FUTURE WORK.

Following a suggestion by the contractor, we will during the remaining contract months use the device geometry shown in fig. 7. This will enable us to devote more time to the following problem areas.

1. Work will be done on the optimization of the bonding procedure with regard to the reverse characteristics of the diodes. Evidently the details of the temperature cycle used during bonding are of critical importance. In addition, we will experiment with various methods of cleaning the diodes prior to bonding.
2. Resistance changes which occur in the metallization during bonding will be further investigated.
3. Some further work will be done on the forward characterization of the silicon-molybdenum contact. Though this is of minor importance at the present time, a better understanding of its potential will be required for guidance to future work.
4. We will determine whether the package as bonded at this time is hermetic. If it turns out to be leaky, the reasons for failure will be investigated.
5. Work to date has been done on p + n junctions. A batch of n + p junctions will be fabricated, and the effect of bonding on the electrical performance of the junctions will be determined.

Table 1. BREAKDOWN VOLTAGES OF VARIOUSLY METALLIZED PLANAR OXIDE.

Slice 11-14-66-1, Mo-Al metallization

400, 330, $>$ 400, 360, 380, $>$ 400, $>$ 400, 300, $>$ 400, 400, 100, 360

Slice 11-15-66-1, Al metallization

350, 350, 370, 300, 300, 250, 300, 300, 300, 250, 350

Slice 10-19-66-1, Al metallization

60, 380, 75, 400, 50, 400, 350, $>$ 400, $>$ 400, 350, $>$ 400, $>$ 400

Slice 09-30-66-1, Cr metallization

300, 400, 400

Table 2. REVERSE CHARACTERISTIC BEFORE AND AFTER METALLIZATION.

Before Metallization			After Metallization		
I/80V	I/120V	BV	I/80V	I/120V	BV
na	na	volts	na	na	volts
27	34	150	12	14	165
28	39	150	12	15	160
28	35	150	48	110	160
25	60	130	210	-	100
24	28	160	14	17	170
22	28	150	-	-	60
20	26	100	-	-	70
25	33	150	13	18	160
14	21	150	-	-	20
16	22	150	16	22	160

Table 3. RESISTANCE CHANGES IN Al LINE ON #7070 DURING TEMPERATURE CYCLING WITH AND WITHOUT VOLTAGE.

#	Temperature ^{o}C	Time min.	Voltage volt	Resistance ohms
1		initial		3.2
	630	10	0	3.2
	630	10	800	4.0
	630	10	800	17.0
2		initial		2.4
	630	10	0	2.4
	630	10	0	2.6
	630	10	0	2.7
3		initial		2.3
	630	10	0	2.2
	630	10	800	2.8
	630	10	800	8.1
	630	10	0	8.1
4		initial		3.2
	630	10	0	3.2
	630	10	1600	3.5
	630	10	1600	4.4

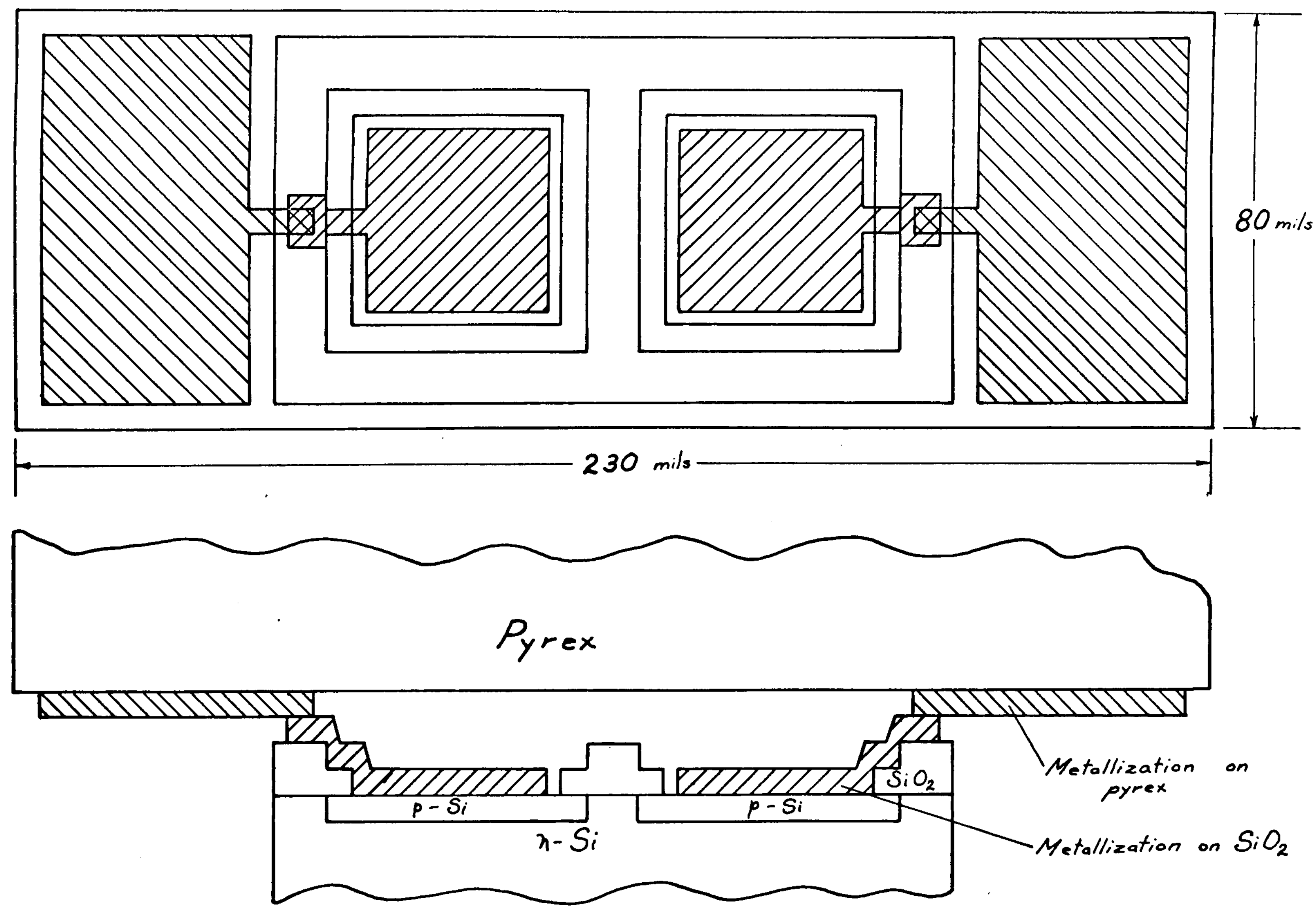

Figure 1. Encapsulation Geometry

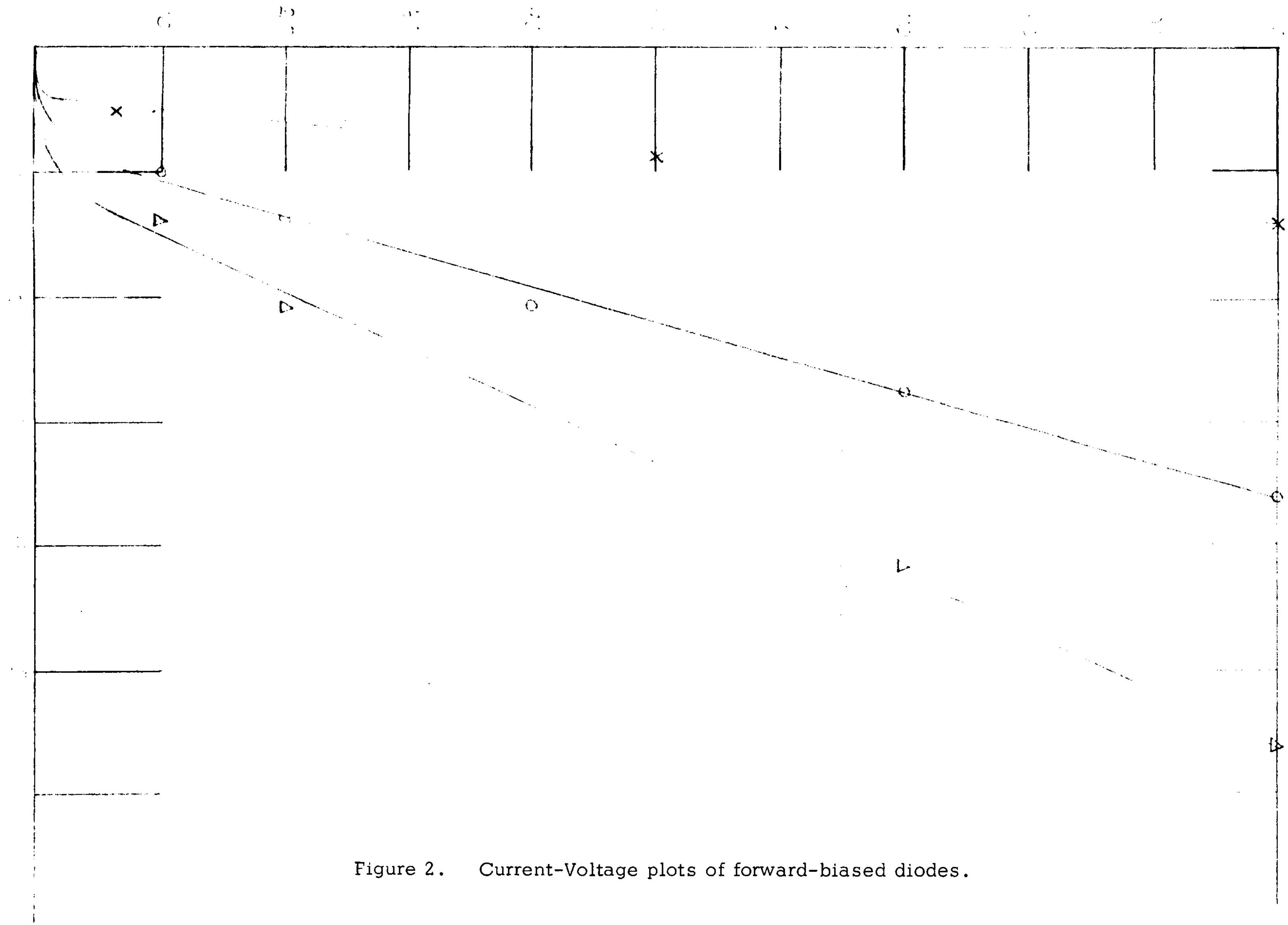

Figure 2. Current-Voltage plots of forward-biased diodes.

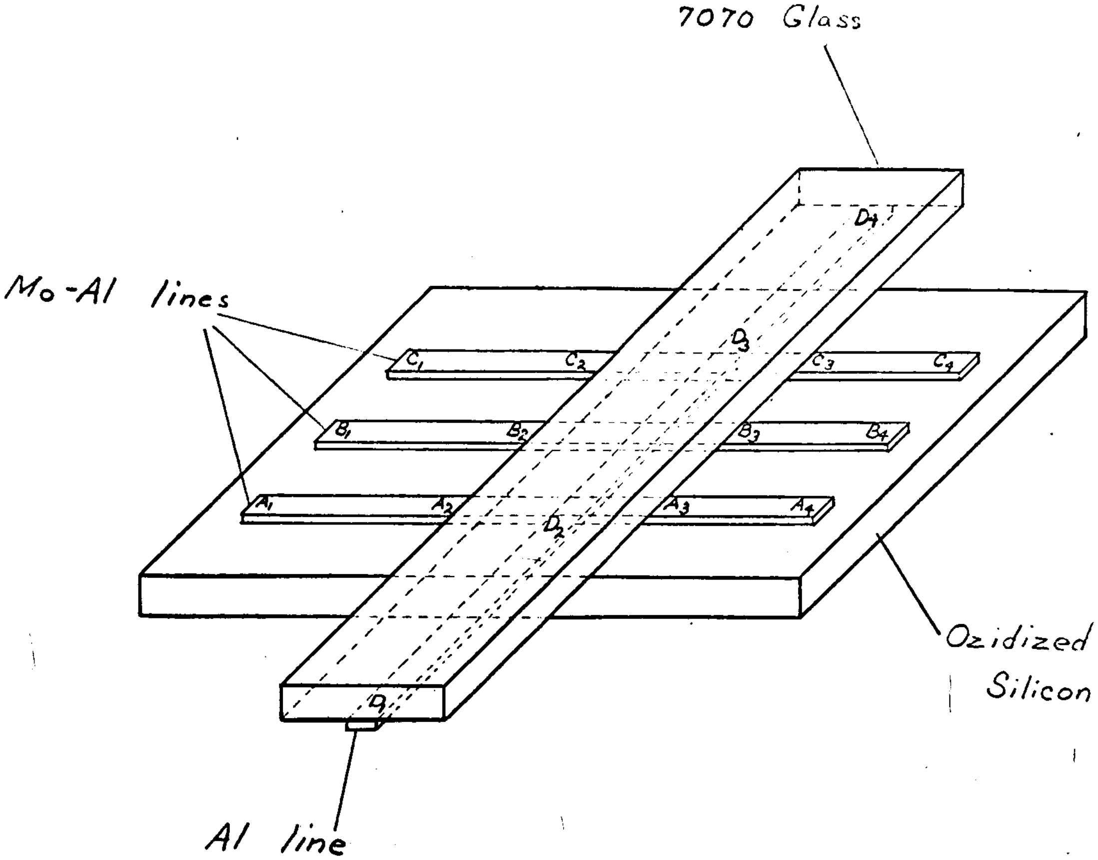

Figure 3. Test vehicle for determination of resistance changes during bonding.

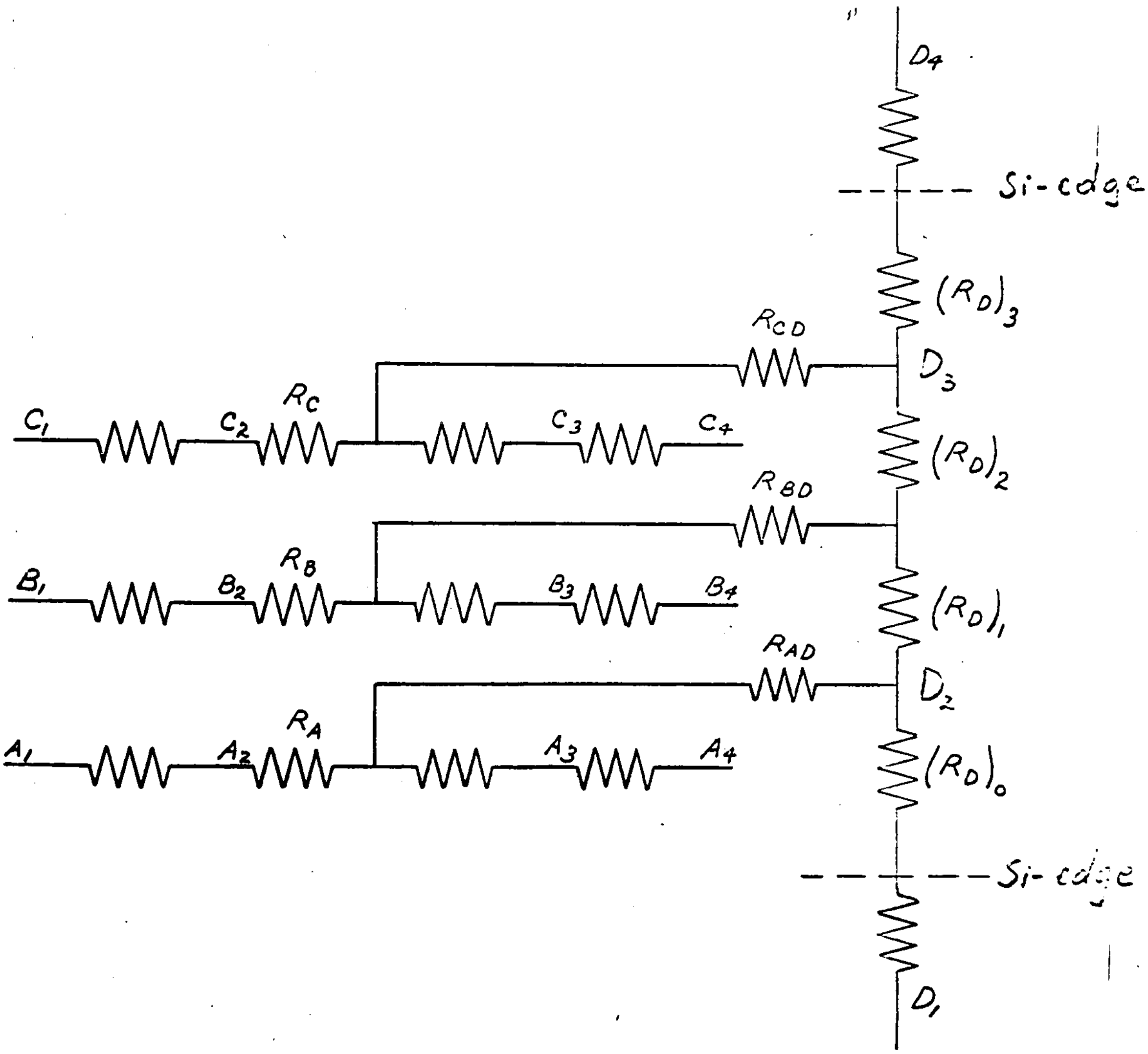

Figure 4. Equivalent circuit used for test vehicle of Figure 3.

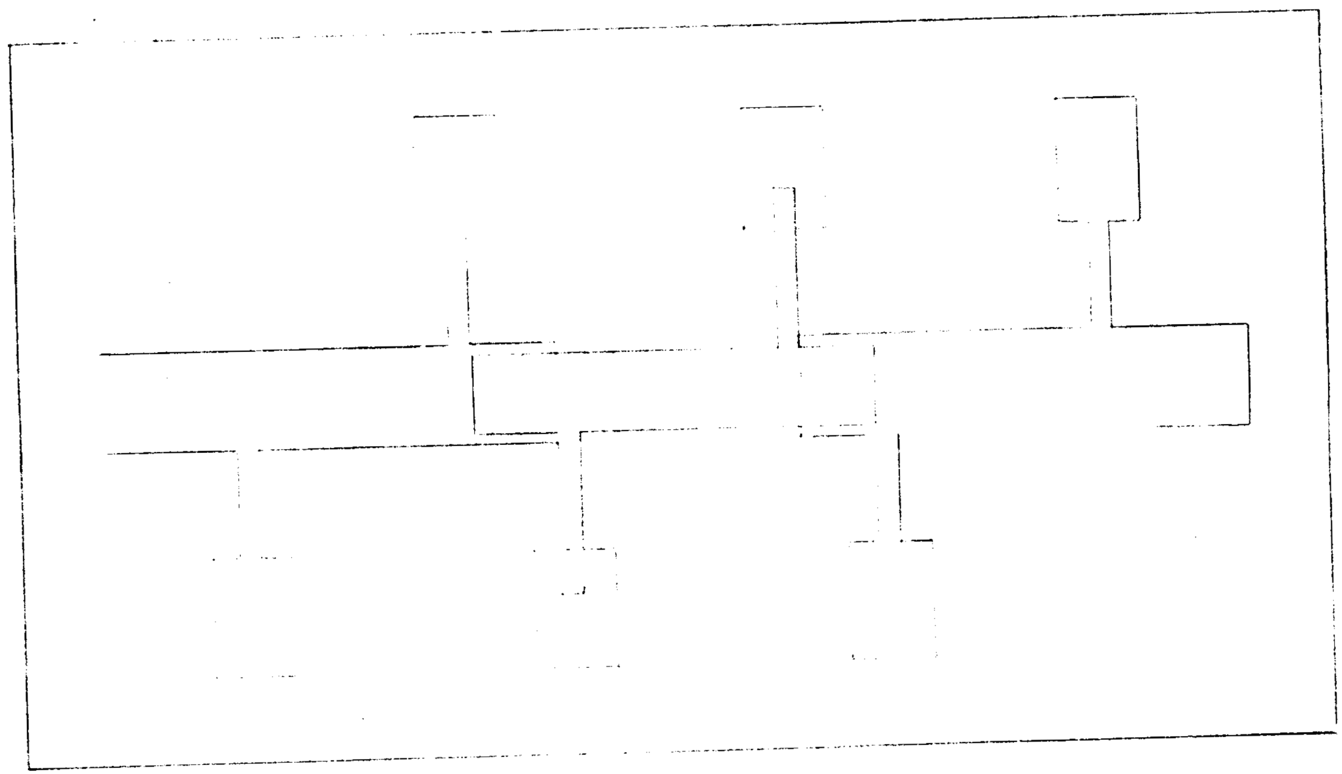

Figure 5. Revised test vehicle for determination of resistance changes in metallization during bonding. Shaded lines represent metallization on glass. Other lines are metallization on oxidized silicon.

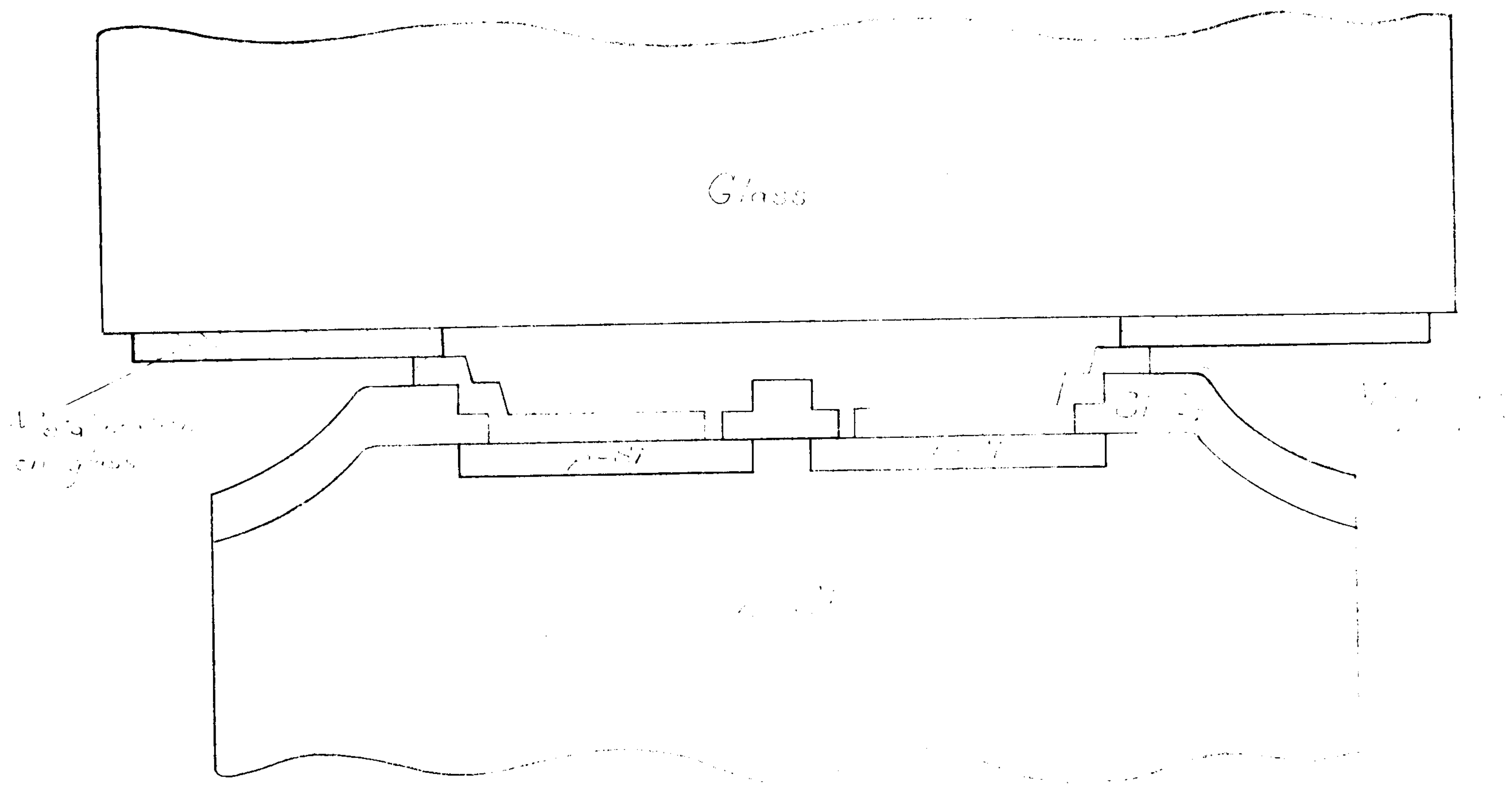

Figure 6. Geometry of bevelled diode.

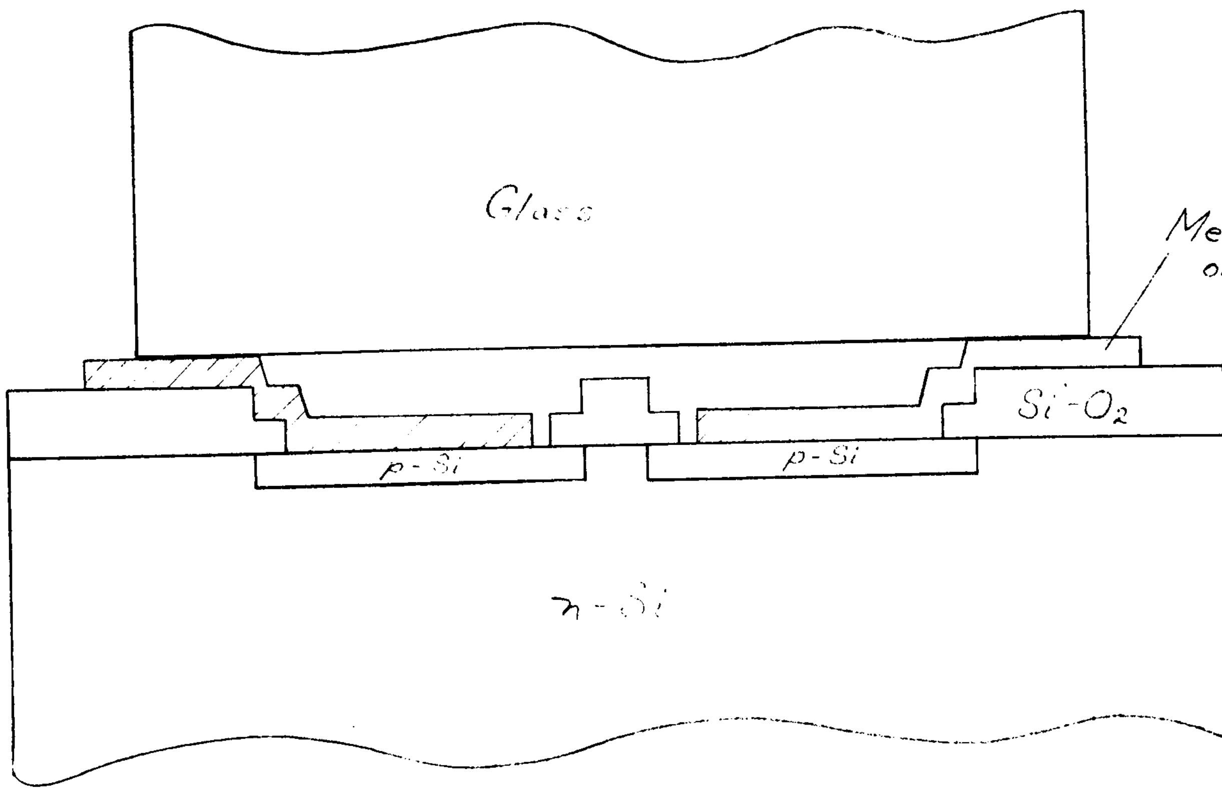

Figure 7. Encapsulation geometry used during 6th contract month.